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A variety of weakly bound and/or metastable molecules have been investigated in the environment of a pulsed supersonic molecular beam. Experiments were attempted with little success for the production of metastable oxygen ring systems. Other experiments focused on metal ion and metal neutral complexes with small molecules or rare gas atoms. Spectrocopic studies were succesful for magnesium ion complexes with the rare gases and with carbon dioxide, water, and nitrogen. Aluminum atom van der Waals complexes were studied with high resolution photoelectron spectroscopy. These studies obtained a variety of new data on metal condensation energetics and the structure of the initial phases of condensation.

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PHOTOGENERATION AND CHARACTERIZATION OF ENERGETIC MOLECULES IN SUPERSONIC MOLECULAR BEAMS

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INTRODUCTION

The goal of this project was to prepare and characterize weakly bound or metastable molecular complexes relevant for the understanding of prospective high energy propellant systems. Two classes of molecules were studied: 1) metastable oxygen ring system, and 2) weakly bound van der Waals or ion-molecule complexes containing light metals (Li, Al, Mg). Both of these classes of molecules are prepared and studied in supersonic molecular beam machines, and they are characterized with laser spectroscopy and time-of-flight mass spectroscopy.

OXYGEN RINGS

Oxygen ring systems were proposed by Schaefer and coworkers to exist as O_4, O_8, and O_{12} metastable ring system analogous to similar sulfur ring systems. High level theoretical calculations indicated that these systems exist as local minima on their respective global energy surfaces, with substantial activation barriers toward decomposition to molecular oxygen. It was therefore the goal of our work to make these systems by condensation of "hot" oxygen plasmas so that these systems might be formed and then to measure their electronic spectra to prove that they exist in the desired metastable ring structures.

Figure 1 shows the mass spectrum obtained when oxygen is pulsed through a supersonic nozzle source and a plasma is ignited by focused laser excitation at 532 nm. As shown, charged O_X species are observed to be formed in this environment. However, from

the mass spectrum alone, it is impossible to distinguish between weakly bound ion-molecule complexes of the form $(O_2)^+$ and the desired covalent species such as O_4^+ and O_8^+. We had planned to pursue electronic spectroscopy on these species under the guidance of the Schaefer group. With our high resolution laser systems, searches for new electronic spectra are prohibitive in time unless the approximate wavelength region for the spectrum can be established in advance. However, the Schaefer group was not able to complete the calculations of excited electronic states for these systems. Therefore, we were not able to complete the spectroscopic characterization of the oxygen ring systems.

LIGHT METAL COMPLEXES

Weakly bound metal complexes are interesting as model systems with which to investigate the possibility of condensation of metal atoms in solid fuel systems. Calculations of the specific impulse of solid hydrogen/solid oxygen systems, for example, are found to be significantly increased upon the addition of metal atoms or metal dimers at roughly the 5% level. These metal-seeded fuel systems appear promising on energetic grounds, but questions remain about the possibility of producing these systems in usable quantities under reasonable conditions. The studies of metal complexes, in our lab and others, makes it possible to measure the interactions (binding energies, etc.) in a finite-sized system, and to evaluate the prospects for scaling up promising systems to larger scales. In the past funding period, we have focused on magnesium ion complexes and on neutral van der Waals complexes of aluminum.

During the past funding period, we have synthesized and studied several magnesium

ion complexes of the form Mg^+-L_x, where L is a small molecule (CO_2, H_2O, N_2, CH_3OH, etc.) or a rare gas atom (Ar, Kr, Xe). These complexes were produced in a specially designed laser vaporization cluster source which produced ionized metal atoms, rather than metal clusters (dimers, trimers, etc.), for condensation with added gases. This general class of systems had not been studied previously in any other labs, but theoretical calculations on these systems were beginning to appear when we first began our work. Various sizes of these metal ion complexes were studied by mass selected photodissociation spectroscopy in a specially designed reflectron time-of-flight mass spectrometer. Photodissociation studies as a function of energy provided information on the energetics of condensation and wavelength dependent photodissociation excitation spectra provided the absorption spectra of the complexes. Electronic transition energies and vibrationally resolved spectra were measured for the complexes Mg^+-Ar, Mg^+-Kr, Mg^+-Xe, Mg^+-CO_2, Mg^+-H_2O (and Mg^+-D_2O), and Mg^+-N_2. As an example, Figure 2 shows the photodissociation electronic spectrum of Mg^+-Ar. The Mg^+-H_2O spectrum was measured with partial rotational resolution. The Mg^+-CO_2 complex was determined to be linear, and the Mg^+-H_2O complex was determined to have C_{2v} symmetry. These are the first, and still the only, polyatomic metal ion complexes for which structures have been determined. The spin-orbit interaction in the $^2\Pi_{1/2,3/2}$ excited state was investigated for the linear complexes formed with the rare gases and CO_2. Table 1 contains a summary of the spectroscopic constants and dissociation energies measured for these various magnesium ion complexes.

In a new development, we have applied a new form of high resolution photoelectron spectroscopy to the study of aluminum-rare gas neutral van der Waals complexes. For these studies, we employed the new techniques of *Mass-Analyzed Threshold Ionization* (MATI)

spectroscopy. The experiments in our lab on Al-Ar were the first ever to use MATI to study a metal cluster molecule. Figure 3 shows the MATI spectrum of Al-Ar, which yields the vibrational structure in the ground electronic state of the $Al\text{-}Ar^+$ ion and also provides the vibrational fundamental for the ground electronic state of the neutral Al-Ar. We are developing MATI for applications to lithium complexes and for the study of metal dimers such as LiAl, LiMg, AlB, etc. These latter systems are also potential candidates for metal seeded fuel systems. The spectroscopic constants for Al-Ar are also given in Table 1.

Table 1. A comparison of the metal-ligand vibrational frequencies (excited state) and dissociation energies of magnesium and aluminum ion complexes.

Complex	Mg^+-L Stretch (cm^{-1})		D_0'' (kcal/mol)		Structure
	Exp.	Theory	Exp.	Theory	
Mg^+-Ar	272	-	3.37	3.25	Diatomic
Mg^+-Kr	258	-	5.2	-	Diatomic
Mg^+-Xe	258	-	11.7	-	Diatomic
Mg^+-CO_2	382	359	14.7	16.4	Linear
Mg^+-H_2O	517	505	25.0	32.2	C_{2v}
Mg^+-N_2	1137		3.03	4.1	Linear
Al^+-Ar	67 (ground state)		2.81		Diatomic

Figure Captions

Figure 1. The mass distribution of oxygen cluster ions generated from a laser plasma.

Figure 2. The photodissociation excitation spectrum of Mg^+-Ar. The spectrum consists of a vibrational progression with each member doubled by the excited state spin-orbit splitting.

Figure 3. The MATI photoelectron spectrum of Al-Ar.

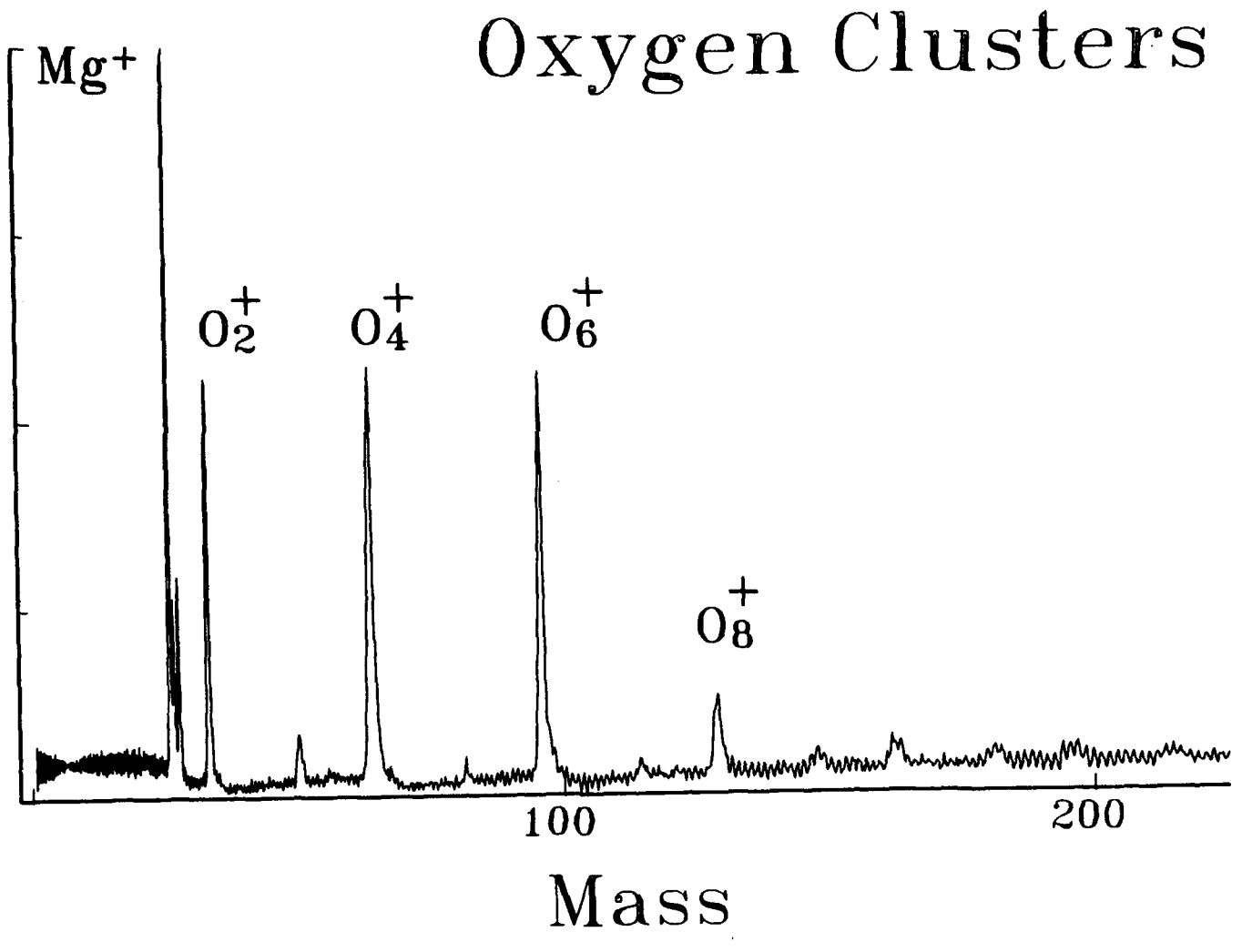

Figure 1.

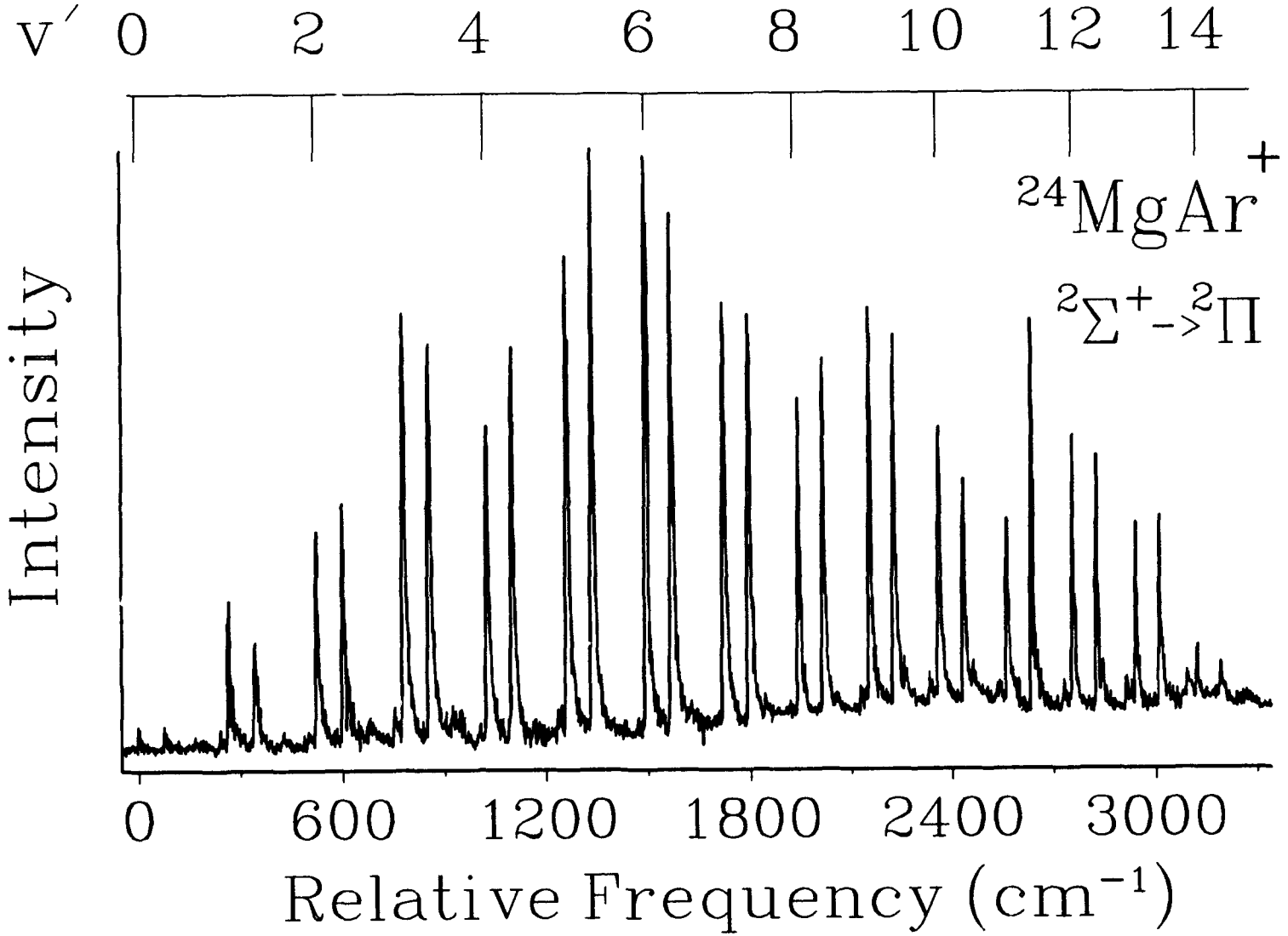
v´ 0 2 4 6 8 10 12 14
$^{24}MgAr^+$
$^2\Sigma^+ -> ^2\Pi$
Intensity
0 600 1200 1800 2400 3000
Relative Frequency (cm^{-1})

Figure 2.

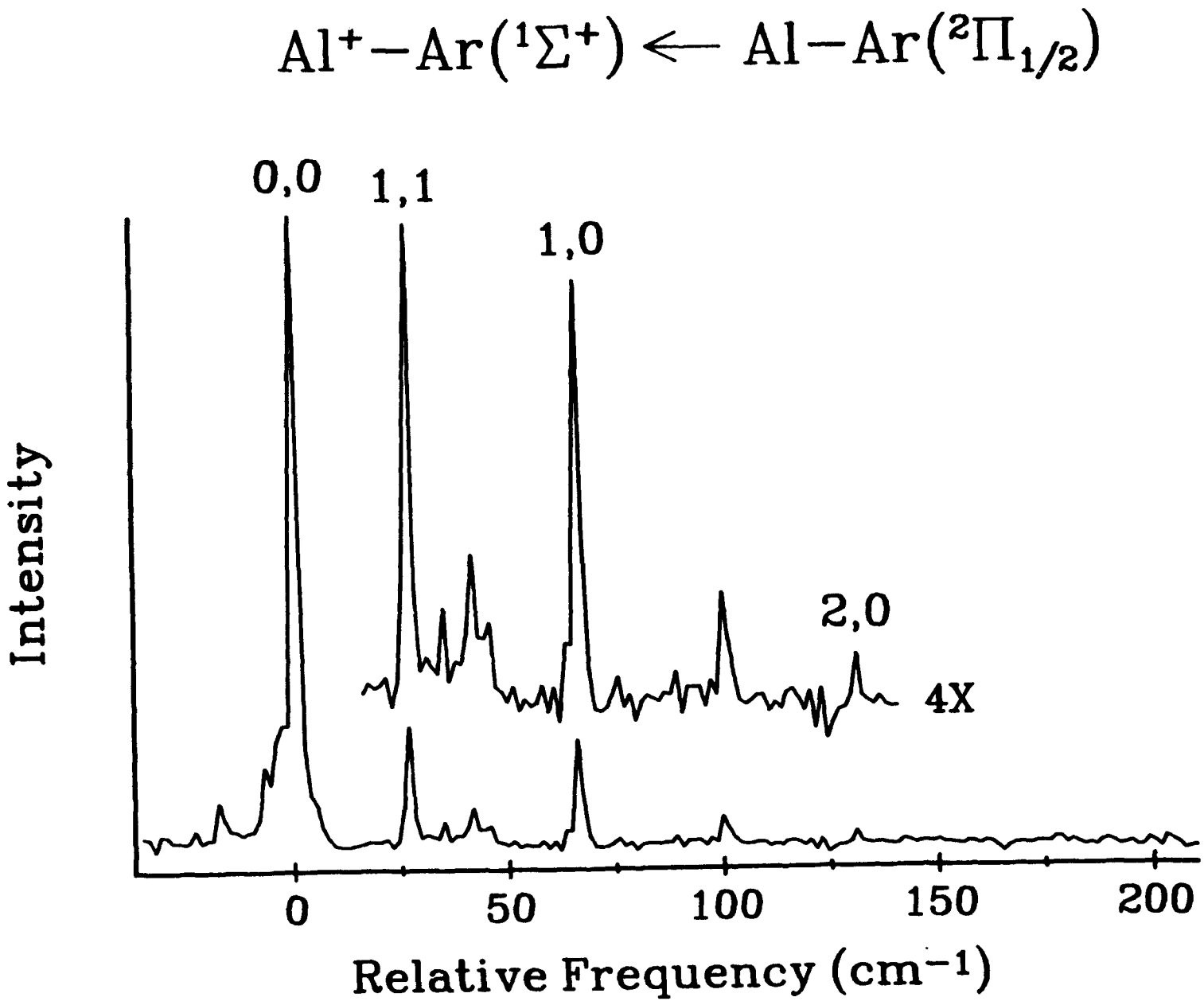
$Al^+-Ar(^1\Sigma^+) \leftarrow Al-Ar(^2\Pi_{1/2})$
0,0
1,1
1,0
2,0
4X
Intensity
0
50
100
150
200
Relative Frequency (cm^{-1})

Figure 3.

Publications Resulting from this Research

1. K.F. Willey, D.L. Robbins, C.S. Yeh and Michael A. Duncan, "Laser Photodissociation Spectroscopy of Mass-Selected Metal Clusters," *Faraday Discussion 92: The Chemistry and Physics of Small Metal Particles*, Faraday Disc. Chem. Soc. 92, 269 (1992).

2. D.S. Cornett, M. Peschke, K. LaiHing, P.Y. Cheng, K.F. Willey and M.A. Duncan, "A Reflectron Time-of-Flight Mass Spectrometer for Laser Photodissociation," *Rev. Sci. Instrum.* 63, 2177 (1992).

3. K.F. Willey, C.S. Yeh, D.L. Robbins and M.A. Duncan, "Photodissociation Spectroscopy of Mg^+-CO_2," *Chem. Phys. Lett.* 192, 179 (1992).

4. C.S. Yeh, K.F. Willey, D.L. Robbins, J.S. Pilgrim and M.A. Duncan, "Photodissociation Spectroscopy of Mg^+-H_2O," *Chem. Phys. Lett.* 196, 233 (1992).

5. C.S. Yeh, K.F. Willey, D.L. Robbins and M.A. Duncan, "Photoinduced Reactions in Collinear Aligned Mg^+-CO_2 Complexes," *J. Phys. Chem.* 96, 7833 (1992).

6. K.F. Willey, C.S. Yeh, D.L. Robbins, J.S. Pilgrim and M.A. Duncan, "Photodissociation Spectroscopy of Mg^+-H_2O and Mg^+-D_2O," *J. Chem. Phys.* 97, 8886 (1992).

7. C.S. Yeh, K.F. Willey, D.L. Robbins and M.A. Duncan, "Photodissociation Spectroscopy of Mg^+-CO_2 and Its Isotopic Analogues," *J. Chem. Phys.* 98, 1867 (1993).

8. J.S. Pilgrim, D.L. Robbins and M.A. Duncan, "Photoionization Electronic Spectroscopy of Al-OH," *Chem. Phys. Lett.* 202, 203 (1993).

9. K.F. Willey, C.S. Yeh and M.A. Duncan, "Mass Analyzed Threshold Ionization Spectroscopy of Al-Ar," *Chem. Phys. Lett.* 211, 156 (1993).

10. J.S. Pilgrim, C.S. Yeh and M.A. Duncan, "Photodissociation Spectroscopy of Mg^+-Ar," *Chem. Phys. Lett.* 210, 322 (1993).

11. K.F. Willey, D.L. Robbins, C.S. Yeh and M.A. Duncan, "Cluster Ion Photodissociation and Spectroscopy in a Reflectron Time-of-Flight Mass Spectrometer," *ACS Symposium Series 549: Time-of-Flight Mass Spectrometry*, R.J. Cotter, ed., American Chemical Society, Washington, DC, 1994, 61.

12. C.S. Yeh, K.F. Willey, D.L. Robbins and M.A. Duncan, "Photodissociation of Magnesium Ion-Molecule Complexes in a Reflectron Time-of-Flight Mass Spectrometer," *Intl. J. Mass Spectrom. and Ion Processes* 131, 307 (1994).

13. J.S. Pilgrim, K. Berry, and M.A. Duncan, "Photodissociation Spectroscopy of Magnesium Ion-Rare Gas Complexes," *J. Chem. Phys.* 100, 7945 (1994).

14. C.S. Yeh, J.S. Pilgrim, D.L. Robbins, K.F. Willey and M.A. Duncan, "Spectroscopy of Weakly-Bound Magnesium Ion Complexes," *Intl. Rev. Phys. Chem.* (invited), in press.

Invited Lectures Presented on this Research

1. "Photochemistry and Spectroscopy of Metal Ion-Molecular Complexes," *XXth Informal Conference on Photochemistry*, Atlanta, GA, April 1992.

2. "Spectroscopy and Photochemistry of Metal Cluster Complexes," Sandia National Laboratories, Livermore, CA, June 1992.

3. "Spectroscopy of Metal Atom and Metal Cluster Complexes," *XIVth International Symposium on Molecular Beams*, Asilomar Conference Center, Pacific Grove, CA, June 1992.

4. "Spectroscopy of Metal Cluster Complexes," Vanderbilt University, June 1992.

5. "Photodissociation and Ion Spectroscopy in a Reflectron Time-of-Flight Mass Spectrometer," *Symposium on Tandem Time-of-Flight Mass Spectrometers*, National Meeting of the American Chemical Society, Washington, DC, August 1992.

6. "Spectroscopy of Metal Cluster Complexes," University of Basel, Basel, Switzerland, October 1992.

7. "Spectroscopy of Metal Cluster Complexes," Technical University of Munich, Garching, Germany, October 1992.

8. "Spectroscopy and Photochemistry of Metal Cluster Complexes," *Physical Chemistry Seminar*, University of California-Berkeley, February 1993.

9. "Spectroscopy and Photochemistry of Metal Cluster Complexes," *Physical Chemistry Seminar*, University of Utah, March 1993.

10. "Studies of Novel Cluster Materials," Battelle Pacific Northwest Laboratories, Richland, Washington, March 1993.

11. "Spectroscopy and Photochemistry of Metal Cluster Complexes," *Departmental Colloquium*, Utah State University, March 1993.

12. "Spectroscopy of Metal Ion Complexes," University of Illinois, Physical Chemistry Seminar, September 1993.

13. "Spectroscopy of Metal Ion Complexes," Purdue University, Physical Chemistry Seminar, September 1993.

14. "Cluster Ion Spectroscopy in a Reflectron Time-of-Flight Mass Spectrometer," *10th Asilomar Conference on Mass Spectrometry*, Estes Park, Colorado, October 1993.

15. "Spectroscopy of Gas Phase Clusters," *Chemistry Colloquium*, University of Alabama-Birmingham, January 1994.

16. Spectroscopy and Photodissociation Dynamics of Metal Cluster Ions," *Physical Chemistry Seminar*, University of California-Irvine, January 1994.

17. "Photodissociation and Photoionization Spectroscopy of Metal Clusters," *SPIE Meeting of the Optical Society of America*, Los Angeles, January 1994.

18. "Spectroscopy and Photochemistry of Metal Cluster Ions," *Physical Chemistry Seminar*, Argonne National Labs, Argonne, IL, February 1994.

19. "Spectroscopy and Photochemistry in Metal Cluster Ions," *Physical Chemistry Seminar*, Northwestern University, February 1994.

20. "Photodissociation of Metal Cluster Ions: From Solvated Ions to Nanocrystals," *Departmental Colloquium*, University of Iowa, February 1994.

21. "Spectroscopy and Photochemistry in Metal Cluster Ions," *Physical Chemistry Seminar*, Iowa State University, February 1994.

22. "Photodissociation Dynamics in Metal Ion-Molecule Cluster Complexes," *Joint Japanese American Cluster Workshop*, Oahu, HW, March 1994.

23. "Photoinduced Chemistry in Metal Ion Cluster Complexes," *Symposium on Cluster Models of Condensed Phased Chemistry*, National Meeting of the American Chemical Society, San Diego, CA, March 1994.

24. "Spectroscopy and Photodissociation of Metal Cluster Ions," *Physical Chemistry Seminar*, University of California-Davis, April 1994.

25. "Photodissociation and Spectroscopy of Metal Cluster Ions," *Physical Chemistry Seminar*, University of Delaware, May 1994.

Poster and Contributed Presentations of this Research

1. M.A. Duncan, "Weak Interactions at Metal Atoms and Clusters Studied with Electronic Spectroscopy in Supersonic Beams," *Air Force Workshop on High Energy Density Materials*, Albuquerque, February 1991.

2. M.A. Duncan, "Mass-Selected Photodissociation Spectroscopy of Metal-Containing Ion-Molecule Complexes," *Gordon Conference on Metal and Semiconductor Clusters*, Wolfboro, NH, August 1991.

3. C.S. Yeh, K.F. Willey, D.L. Robbins, J.E. Salcido and M.A. Duncan, "Photoinitiated Reactions in Mass-Selected Magnesium Ion-Molecule Complexes," *XXth Informal Conference on Photochemistry*, Atlanta, GA, April 1992.

4. J.E. Pilgrim and M.A. Duncan, "A Pulsed Electrical Discharge Metal Cluster Source," *XXth Informal Conference on Photochemistry*, Atlanta, GA, April 1992.

5. M.A. Duncan, "Photodissociation Spectroscopy of Magnesium Ion-Molecule Complexes," *Gordon Conference on Molecular and Ionic Clusters*, Irsee, Germany, October 1992.

6. M.A. Duncan, "Photodissociation Spectroscopy of Metal Containing Ion-Molecule Complexes," *Gordon Conference on the Structures, Energetics, and Reaction Dynamics of Gaseous Ions*, Ventura, CA, March 1993.

7. M.A. Duncan, "Spectroscopic Studies of Novel Metal Complexes," *Air Force Office of Scientific Research, High Energy Density Materials (HEDM) Program Contractor's Meeting*, Woods Hole, MA, June 1993.

8. K.F. Willey, C.S. Yeh and M.A. Duncan, "Characterization of the Ground State of Al^+-Ar Using a New Configuration of Mass Analyzed Threshold Ionization (MATI)," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, Ohio, June 1993.

9. C.S. Yeh, K.F. Willey, D.L. Robbins, J.S. Pilgrim and M.A. Duncan, "Photodissociation Spectroscopy of the Mg^+-CO_2 Complex and Its Isotopic Analogs," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, Ohio, June 1993.

10. K.F. Willey, C.S. Yeh, D.L. Robbins, J.S. Pilgrim and M.A. Duncan, "Photodissociation Spectroscopy of Mg^+-H_2O and Mg^+-D_2O," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, Ohio, June 1993.

11. J.S. Pilgrim, D.L. Robbins and M.A. Duncan, "Photoionization Electronic Spectroscopy of AlOH," *Ohio State International Symposium on Molecular Spectroscopy*, Columbus, Ohio, June 1993.